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Comparative Review of High- and Low-Temperature Electrochemical Ammonia Synthesis

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ABSTRACT

Electrochemical nitrogen reduction reaction (eNRR) is an emerging field in sustainable chemistry. This review explores the advancements and challenges in both low-temperature (LT) and high-temperature (HT) eNRR methodologies, including aqueous systems, solid-state synthesis, and molten salt techniques. The primary challenges in eNRR are sufficient selectivity and energy efficiency with reliable data acquisition, especially in terms of false positive results. This review explores the current state of eNRR research, emphasizing the ongoing difficulties in improving both the efficiency and reliability of low-temperature aqueous systems. We highlight the potential of lithium-mediated systems in molten salts and organic solvents, which currently demonstrate considerable promise for industrial application, although energy efficiency remains a significant challenge. The review underscores the need for rigorous testing and more consistent research methodologies. This comprehensive analysis places recent advances in eNRR in the broader context of sustainable ammonia synthesis. It emphasizes the importance of continued innovation, standardized research practices, and collaborative validation efforts across different laboratories. In conclusion, while the eNRR field is evolving, a unified approach in research and validation is essential to overcome existing challenges. The successful development and implementation of eNRR technologies, especially lithium-mediated methods, could revolutionize global ammonia production, offering a sustainable alternative to the conventional Haber–Bosch process.

1 | Introduction

Ammonia (NH_3) plays a vital role in various industrial sectors, particularly in the production of fertilizers, supporting global food security [1]. It serves as a versatile raw material in the manufacturing of a wide range of chemical compounds, from explosives to pharmaceuticals [2]. Moreover, the significance of ammonia extends to clean energy applications, where it has the potential to be a crucial transportable energy source due to its energy density, ease of storage, and well-established global transportation [3, 4]. The global production of ammonia currently amounts to approximately 240 million tons with an annual growth rate of 4%, making it one of the most produced chemicals in the world [5]. Thus, ammonia production will continue to play an important role in the future. The Haber–Bosch (HB) process as the conventional production method, while indispensable, poses significant challenges, primarily characterized by its high-energy requirements and substantial carbon footprint. Around 1.8% of

Abbreviations: CE, current efficiency; eNRR, electrochemical nitrogen reduction reaction; GDC, gadolinium-doped ceria; HB, Haber–Bosch; HER, hydrogen evolution reaction; HT, high-temperature; KPI, key performance indicators; LT, low-temperature; MEA, membrane electrode assembly; NEMCA, non-faradaic electrochemical modification of catalytic activity; SEI, solid–electrolyte interphase; SOEC-H, proton conducting solid oxide electrolysis cell; SOEC-O, oxide-ion conducting solid oxide electrolysis cell; SSAS, solid-state ammonia synthesis; TEA, techno-economic analysis; THF, tetrahydrofuran; TRL, technology readiness level; YSZ, yttrium-stabilized zirconia.

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global carbon dioxide (CO_2) emissions today are caused by the production of ammonia via HB [6]. As alternative approach, electrochemical ammonia synthesis has gained recognition as a potential path-breaking technology [7]. In particular, the electrochemical dinitrogen reduction has emerged as an alternative to the energy-intensive HB process for ammonia synthesis [8]. This technology includes high-temperature (HT) and low-temperature (LT) applications [9]. HT approaches include direct reduction of nitrogen at the electrode using solid state electrolytes, molten salts or indirect reduction with molten salts [9]. On the other hand, LT methods involve direct reduction with aqueous electrolytes, membrane electrode assemblies (MEA), or non-aqueous electrolytes like organic solvents or ionic liquids [7, 10, 11]. They also include indirect methods such as the lithium-mediated shuttle, which uses lithium in an organic solvent to facilitate the reaction [12]. This development has sparked global research interest, leading to the publication of numerous experimental and theoretical studies. Despite its potential, the field of eNRR faces challenges due to the prevalence of false positive results [13]. Here, we aim to provide an overview of the current state of research regarding the eNRR for ammonia synthesis. Additionally, this review conducts a comparative examination of LT and HT approaches. Driven by the intention to clarify the research landscape, pinpoint areas with promising potential, and offer a comprehensive overview of eNRR research for researchers in the field we spotlight the progress, obstacles, and recent developments. By comparing HT and LT eNRR technologies, this review combines insights from both fields to identify key trends and research gaps. It further examines the reliability of existing data by incorporating recent findings on false positives and experimental inconsistencies, contributing to the advancement of future studies. This work provides practical guidance for researchers working in the evolving field of sustainable ammonia synthesis.

2 | Thermodynamics of Ammonia Synthesis

To form ammonia, sources of nitrogen and hydrogen are necessary. In the case of eNRR, the nitrogen source is dinitrogen (N_2). The source of hydrogen or protons depends on the technology. In aqueous eNRR liquid water serves as the proton source, while in all other technologies, it can be liquid water or hydrogen [14]. For HT applications, mainly steam or hydrogen is used [9]. Alternative sources may include carbon-containing substances like methane inorganic compounds like hydrogen sulfide or hydrogen chloride [15–18]. However, these are not considered in this review for two reasons: first, they are rarely used in literature, with a few exceptions. Second, the carbon atoms in these sources could potentially lead to CO_2 emissions, contradicting the sustainability aspect of the technology. The reactions for both systems are:

$$3H_2O_{(l,g)} + N_{2(g)} \longrightarrow 2NH_{3(g)} + 1.5O_{2(g)} \quad (1)$$

$$3H_{2(g)} + N_{2(g)} \longrightarrow 2NH_{3(g)}. \quad (2)$$

The Gibbs free energy of formation ΔG_f can be calculated from the enthalpy of formation ΔH_f, the temperature T, and the entropy ΔS_f by [19]:

$$\Delta G = \Delta H - T\Delta S. \quad (3)$$

The standard potential or reversible cell voltage of a reaction can be calculated from ΔG_f Equation 4 where n is the number of electrons involved in the reaction and F is the Faraday constant [19].

$$E_f = -\frac{\Delta G_f}{nF} \quad (4)$$

ΔH_f is the total energy demand of the reaction which can be provided in form of heat $T\Delta S_f$ and electrical energy ΔG_f. Figure 1 shows the total energy demand ΔH, required potential ΔG and heat demand $T\Delta S$ for Reactions (1) and (2). Because Reaction (2) is exothermic, its enthalpy of formation is negative. ΔG_f is negative below 180°C, indicating that the reaction occurs spontaneously. As the temperature increases, ΔG_f becomes less negative, and consequently, E_f decreases, meaning that HTs are unfavorable for this reaction. On the other hand, Reaction (1) is an endothermic and endergonic reaction ($\Delta H_f > 0$, $\Delta G_f > 0$,). Between 0 and 100°C ΔG_f decreases, meaning higher temperatures within this range lower the required potential. Above 100°C this trend reverses, and around 420°C the same potential at room temperature is needed. The discontinuity in ΔH_f and $T\Delta S$ arises from the assumption that water (H_2O) enters the process in gaseous form for temperatures above 100°C. However, the overall process energy must also include the energy needed to vaporize water. For Reaction (1), there is an optimal temperature at 100°C, where the energy required is minimal, increasing at both lower and higher temperatures. In Figure 1, ΔH_f, ΔG_f, and $T\Delta S$ are also plotted for the hydrogen evolution reaction (HER), the main side reaction:

$$2H_2O \longrightarrow 2H_2 + O_2. \quad (5)$$

As shown in the diagram, ΔG_f and thus E_f are lower than for Reaction (1). This means that the HER is favored compared to eNRR. For the HER, E_f decreases with increasing temperature. From a thermodynamic point of view, this effect increases with increasing temperature. The standard enthalpy and standard entropy required for the calculations were obtained from the NIST database [20]. In addition to the thermodynamic considerations, the reaction pathways play a critical role in determining the feasibility and efficiency of eNRR [21]. While this review primarily focuses on experimental advancements and results in eNRR technologies, it is important to briefly outline the underlying reaction mechanisms. These pathways can be broadly categorized into direct nitrogen reduction at the electrode surface and indirect mechanisms, such as lithium-mediated processes, where intermediates like lithium nitride facilitate ammonia synthesis. Each pathway presents unique challenges and opportunities, influencing key factors like energy efficiency (EE) and selectivity. For a more detailed exploration of the reaction pathways, readers are referred to the reviews of Chen et al. [22], Liu et al. [23], and Qiang et al. [24].

3 | Technologies

The eNRR technologies can be divided into HT and LT applications [9]. Each can be subdivided into direct and indirect nitrogen reduction. In direct reduction, nitrogen is reduced at the electrode. In indirect nitrogen reduction, a mediator is reduced which

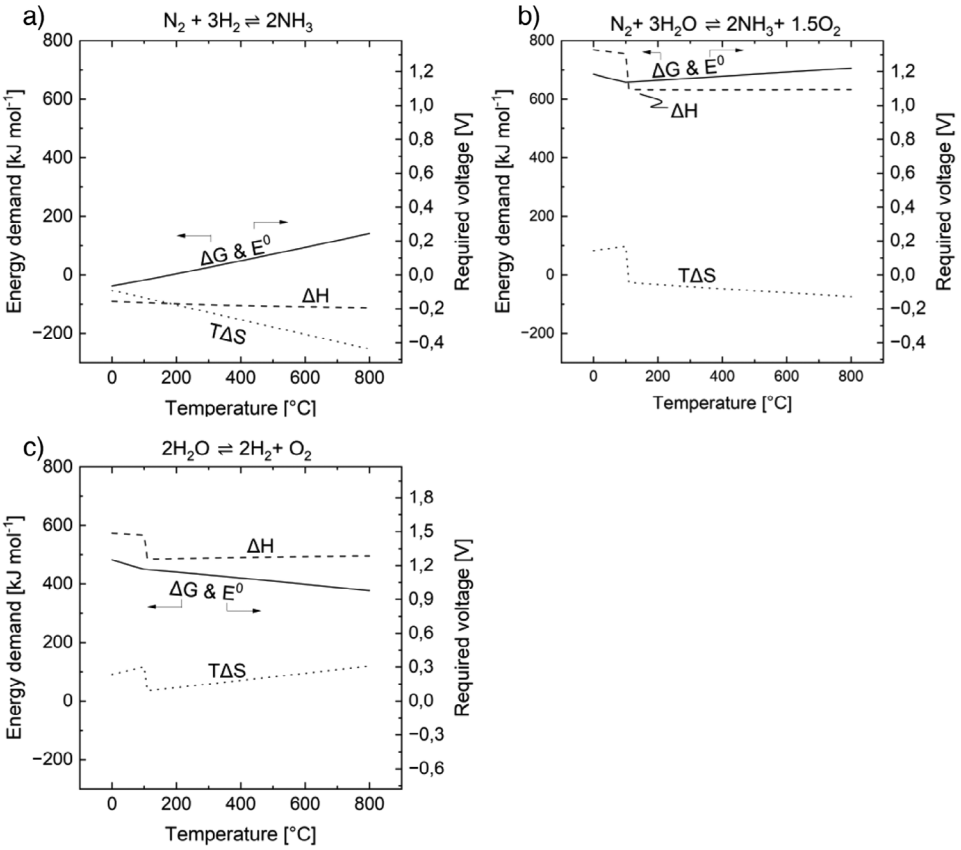

FIGURE 1 | Enthalpy of formation ΔH, Gibbs free energy ΔG, heat demand $T\Delta S$, and standard potential E^0 for the reaction of hydrogen to ammonia (Reaction 2, a), water to ammonia (Reaction 1, b), and the competing HER (Reaction 5, c). The required voltage was calculated from the Gibbs free energy (Equation 4) with the standard enthalpy and standard entropy obtained from NIST database [20].

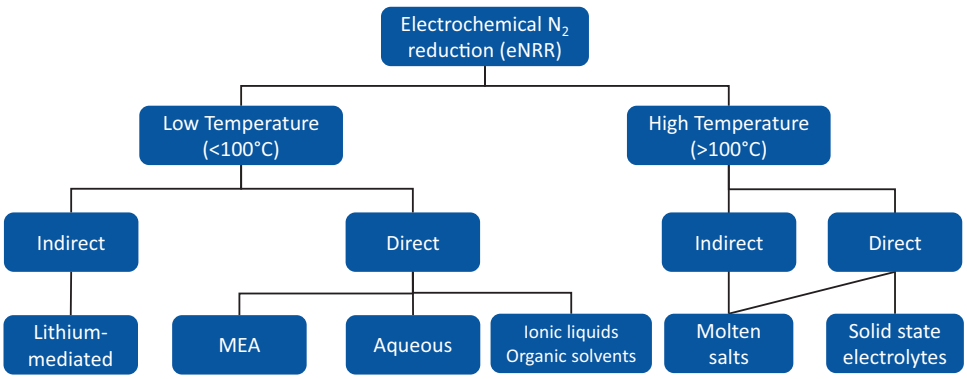

FIGURE 2 | Overview over high- and low-temperature technologies in eNRR categorized in direct and indirect reduction. Direct refers to the reduction of N_2 at the electrode surface, while indirect refers to the reduction of nitrogen by a mediator, usually lithium. For molten salts both variants were reported.

subsequently reacts with nitrogen. The mediator is regenerated at the anode. Direct LT applications can be categorized into systems with aqueous electrolytes, MEAs, and systems with non-aqueous electrolytes such as organic solvents or ionic liquids. An overview is given in Figure 2.

Aqueous electrolytes and MEAs are combined in this review due to their similar technological status and challenges. In the case of indirect LT application, we refer to the so-called lithium-mediated shuttle, where lithium is used in an organic solvent [12]. In HT eNRR, both direct and indirect methods exist. Molten salts in HT eNRR can be classified into either category, depending on the publication. There are applications where lithium is used as a mediator, but also cases where nitrogen is intended to be directly reduced at the electrode [25]. Another direct HT method is solid-state ammonia synthesis (SSAS), predominantly using ceramic electrolytes [9]. The individual technologies, the current state of the art, and future challenges are discussed in the following.

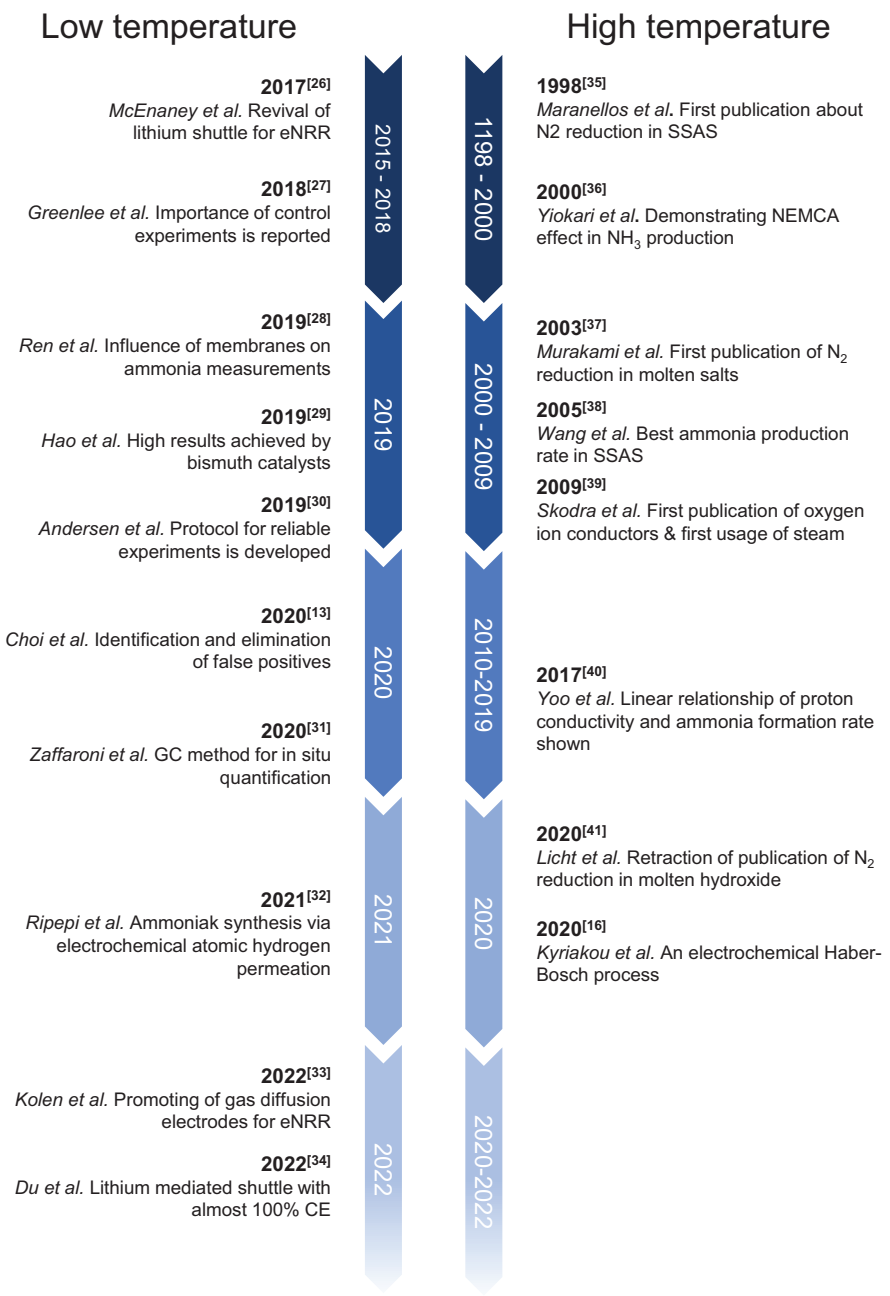

FIGURE 3 | Timeline of important publications in the field of high- and low-temperature electrochemical ammonia synthesis. (LT: [13, 26–34] HT: [16, 35–41]).

A timeline with relevant publications in LT and HT is given in Figure 3.

3.1 | Aqueous Systems

Among all the potential systems for electrochemical ammonia synthesis, aqueous systems at ambient conditions have received the most attention, as evidenced by the number of publications. This can be attributed to the relatively simple experimental setups required, feasible in most laboratories. Various materials have been explored for eNRR, including single-atom, noble metal, transition metal, transition metal compounds like metal nitrides, metal oxides, and metal organic frameworks, alloys, and metal-free materials like carbon or polymer catalysts [23, 42, 43]. In these systems, acidic, neutral, and basic electrolytes are employed, typically with concentrations ranging from 0.05 molar to 0.5 molar, and frequently 0.1 molar [10, 44]. Commonly used electrolytes include KOH, HCL, Na_2SO_4, and H_2SO_4 [10, 44]. The significant potential of this technology has motivated numerous global research groups to investigate eNRR in aqueous environments. Over recent years, hundreds of experimental and theoretical studies have been conducted [10, 13]. The involvement of various research institutions in a particular field generally promises significant advancements and rapid progress in the development of the technique. Unfortunately, in the case of eNRR, the research landscape has become increasingly complex and challenging. This complexity stems from technical hurdles

but also from the overwhelming number of publications, many of which do not precisely reflect the current state of research regarding experimental protocols and control experiments. As a result, only a minority of these publications can be deemed relevant and reliable [10, 13].

eNRR faces several technical challenges, due to the strong triple bond of dinitrogen, which must be broken to form ammonia [45]. Additionally, the low solubility of nitrogen in water limits its availability at the electrode surface. The issue of low solubility can be addressed by using gas diffusion electrodes, a common strategy in CO_2 reduction [46]. However, the strong binding energy remains the most significant obstacle. To date, no catalyst has been successfully developed that achieves high selectivity or yield rate. In 2016, the U.S. Department of Energy set a goal of achieving 90% current efficiency (CE) at a current density of 300 mA/cm^2, a target that has yet to be met [47]. It remains to be proven whether eNRR can be conducted under ambient conditions in aqueous media with sufficiently high yield rate.

Reports of false positives began to emerge as in 2017. Shipman et al. [48] attempted to reproduce the results of a study claiming an active catalyst for eNRR. They observed similar amounts of ammonia when conducting experiments under both N_2 and Ar supply while in the original publication, the catalyst was only investigated with N_2. Shipman et al. [48] deduced that the measured ammonia during the experiment is not the result of N_2 reduction but arises from the decomposition of the nitrogen-containing catalyst.

In the following year, Greenlee et al. [27] published a comprehensive review with a focus on control experiments in the context of eNRR. Their initiative originated from their own experiments, which yielded significant ammonia production in control experiments involving argon. As a result, the authors proposed three recommendations to ensure reliable research in this field. First, they stressed the importance of meticulously documenting and publishing reference experiments. Second, they advocated for the application of secondary validations, such as experiments with isotope-labeled nitrogen. Lastly, they highlighted the importance of disclosing the measurement accuracy of analytical methods used in the studies.

In 2019, a large number of publications on possible false positives and their causes were published [49–56]. According to these publications, false positive results can arise according to two different principles. The first principle involves direct introduction of ammonia into the experimental setup, for example, via absorption and subsequent desorption of exogenous ammonia on surfaces like cell walls, electrodes, or membranes. Additionally, ammonia can enter the system through impure gas streams or as a contaminant in the electrolyte. A less noted but possible source is membranes, which can absorb and later release ammonia, thereby contaminating the system [28, 57]. The second principle of false positives is the conversion of nitrogen compounds other than N_2. This includes the decomposition of nitrogen-containing catalysts if only the reduction step occurs without subsequent reoxidation, as described by the Mars–van-Krevelen mechanism [58]. Furthermore, the reduction of NO_x compounds can occur [59]. These NO_x compounds can be introduced through impure gas streams or electrolytes, or by adsorption to surfaces or the catalyst. During the experiment, these oxides undergo reduction, leading to an increase in observed ammonia concentration, even in the absence of N_2 reduction. The possible sources for false positives are summarized in Figure 4.

The abundance of potential contaminants combined with notably low-production rates has transformed the eNRR research domain from being easily accessible to a highly complex domain with numerous limitations and challenges. The main challenge lies in the need to detect and eliminate all potential contaminations, which requires the execution of extensive control experiments and sophisticated analytical procedures. To establish a foundation for reliable and comparable experiments within the research community, guidelines for conducting and reporting experiments have been developed [30, 54, 57]. The probably most cited protocol among these was published by Andersen et al. [30]. The developed protocol addresses the primary sources of false positives and serves as a comprehensive guide for validating N_2 reduction. Nonetheless, numerous papers are still published without adequate control experiments and well-defined experimental protocols.

A particularly challenging aspect in this context is the reliable quantification of ammonia as a result of its extremely low concentrations. Zhao et al. [60] and Utomo et al. [61] conducted a comparative study on various methods for ammonia detection within eNRR-relevant concentration ranges, specifically evaluating the iodophenol blue method, Nessler's reagent method, ion chromatography, and ^{1}H nuclear magnetic resonance. Additional methods, such as fluorometric methods, ion-selective electrode methods, enzymatic approaches, conductive techniques, and titrimetric methods, have also been investigated. Furthermore, there are investigations into specific methods, such as the widely used iodophenol blue method studied by Biswas et al. [62], the application of ion chromatography analyzed by Duan et al. [63] and Bragulla et al. [64], or nuclear magnetic resonance investigated by Assafiri et al. [65]. Utomo et al. [61] concluded in their study that the choice of detection method heavily depends on the sample matrix, which can vary across different eNRR technologies. Zhao et al. [60] emphasized that detecting ammonia concentrations below 0.2 ppm is error-prone, which is likely true for most photocatalytic or electrocatalytic NH_3 synthesis experiments. They also stressed that reliable quantification is highly dependent on the adherence to standardized protocols.

In 2020, Choi et al. [13] conducted a study evaluating 127 eNRR publications against three criteria for experimental rigor. The criteria were (I) sufficiently high yield rate, (II) reliable and sufficient $^{15}N_2$ control experiments, and (III) rigorous control and quantification of nitrogen oxides. None of the publications examined met all three criteria. Therefore, the authors concluded that the direct eNRR to ammonia remains unproven. The study by Choi et al. [13] included research up until April 2020. At that time, publications on experimental protocols and false positives were relatively new, which explains the results of the study's findings as a reflection the state of research at that time. However, a similar study was conducted in 2023 by Rezaie et al. [10], applying comparable criteria. The authors weighted the yield rate and control experiments in a probability matrix and thereby investigated the probability of reliability of eNRR studies. This study examined 233 works from 2020 to 2022 involving isotope labeling

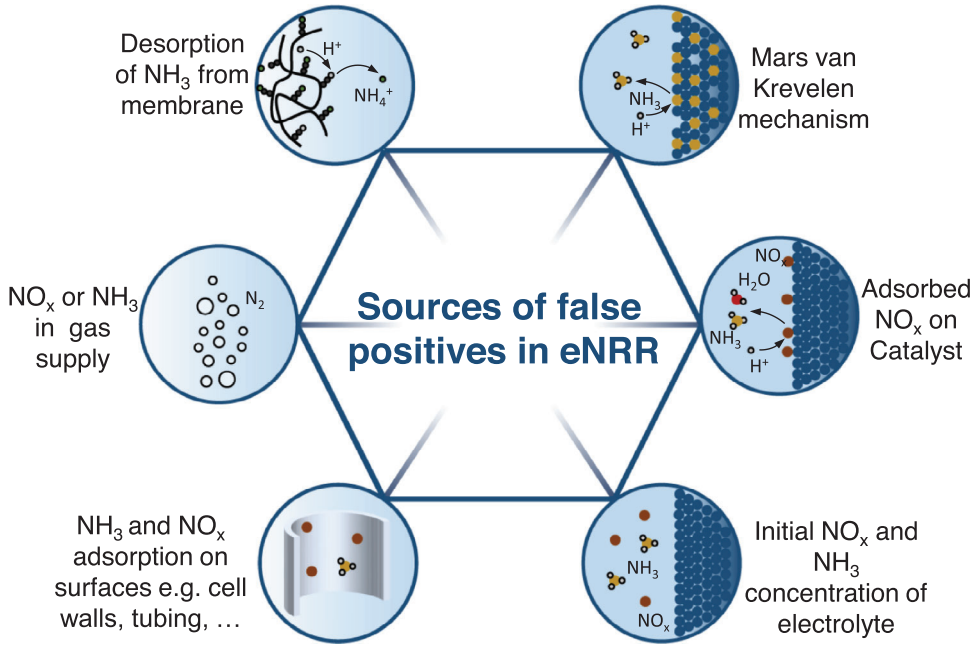

FIGURE 4 | Summary of sources of false positive results in eNRR. eNRR, Electrochemical nitrogen reduction reaction.

experiments in aqueous media. Only 13 of these were classified as very likely reliable. However, to conclusively prove eNRR in aqueous media under environmental conditions, an in-depth evaluation of experimental results for potential contaminations is essential. Additionally, we propose that at least one independent laboratory is necessary for validation. Notably, none of the studies achieved production rates exceeding 10 nmol/cm^2/s, a threshold established by Choi et al. [13] as a criterion for highly plausible and promising production rates. It is important to recognize that this threshold lacks a fundamental basis and primarily serves as a reference point. Nevertheless, it underscores the fact that eNRR research is still far from substantial progress toward higher technology readiness levels (TRLs).

The considerable challenges in electrochemical ammonia synthesis underline the need for rigorous control experiments, detailed experimental evaluation regarding possible contaminations, and the reproducibility of results across research groups. We therefore recommend that all future research in this field be published only if it aligns with the latest insights on potential false positives. Ideally, findings should be verified and confirmed by an independent second authority before publication.

3.2 | Non-Aqueous Electrolytes

To address the primary challenges of eNRR under ambient conditions, particularly low nitrogen solubility and the competitive HER, researchers explored alternative, non-aqueous electrolytes. In their perspective Singh et al. [7] identified non-aqueous electrolytes as a crucial experimental condition for eNRR, beneficial to suppress the HER. One of the most extensively studied classes of substances in this context are ionic liquids, particularly phosphonium-based or pyrrolidinium-based ionic liquids like [C4mpyr][eFAP]. They are used either in their pure form or dissolved in fluorinated solvents [66]. Their characteristics, such as high thermal stability, ionic conductivity, and electrochemical stability, make them suitable for various electrochemical processes [67]. Furthermore, the properties of ionic liquids can be tailored to meet specific needs due to the numerous possible combinations of salts. The potential of ionic liquids to control the availability of protons, thereby influencing HER, has been the subject of research [68]. Their high nitrogen solubility [69–72] is another factor that makes them a promising candidate for eNRR.

Zhou et al. [73] conducted one of the first studies to apply a non-aqueous electrolyte, achieving a low yield rate of about 0.023 nmol/cm^2/s. By varying the ionic liquid, they reached a CE of 60% at lower yield rates. A similar yield rate with a CE of 32% was achieved 1 year later in 2018 by Suryanto et al. [66]. At the time of these publications, awareness of possible false positive results in NRR was emerging, but comprehensive test protocols and control experiments based on current literature were not yet established. These protocols were developed in later publications by the same research group around MacFarlane and Simonov [13, 56].

In 2020, the same group investigated a molybdenum catalyst in both aqueous media and an ionic liquid for the eNRR activity [74]. They observed that the catalyst was inactive in the aqueous electrolyte, aligning with theoretical predictions. Ammonia formation in the non-aqueous electrolyte was confirmed, but was found to be largely independent of water concentration, N_2 pressure, and applied potential. Adsorbed ammonia was detected at the electrode, so the authors concluded that the ammonia formed in the initial phase of the experiments adsorbed at the electrode surface, blocking the active sites of the catalyst and halting further ammonia production. This study included improved NO_x control and partial gas scrubbing for the gas supply, but lacked complete gas scrubbing and N^{15} isotope experiments. The NO_x concentration during experiments was high relative to the amount of ammonia produced, indicating a potentially

significant impact on the overall ammonia yield. This led authors to conclude that exclusive ammonia formation from N_2 reduction could not be confirmed.

In 2021, the group published another paper focusing on potential false positives, particularly regarding NO_x reduction, in non-aqueous electrolytes [75]. They detail the possible causes of NO_x accumulation in the system, including the affinity of certain ionic liquids to absorb NO_x from ambient air and adsorption onto surfaces such as cell walls and electrodes. They found that even if known impurities are controlled, a constant, undetectable impurity is introduced via the gas supply, likely adsorbing on the electrode surface and releasing upon potential application. Therefore, NO_x detection should be performed not only prior to but also during the experiment. With these findings, new possibilities for the occurrence of false positives were presented. The authors point out that the results of their previous publications might be affected [66, 73]. In summary, no activity of the used iron catalyst could be detected in the electrolyte, which consisted of a mixture of ionic liquid and acetonitrile. Drawing from the acquired knowledge, the authors conclude that results in the field of eNRR may be questionable even if $^{15}N_2$ control experiments have been conducted, but the measured production rate is below 0.1 nmol/cm^2/s.

Apart from the studies in ionic liquids, there are two publications in non-aqueous media, more precisely in ethylenediamine and in 2-propanol [76, 77]. However, both publications date back to 2016, predating awareness of possible false positives. The results achieved should therefore be reproduced before further utilization, taking into account the most recent findings.

To the best of our knowledge, there is no research that has conclusively proven successful eNRR in non-aqueous environments. The only exception to this relates to the study of the 'lithium-mediated shuttle', which are covered in the following section. So far, catalysts have predominantly included transition metals such as iron, nickel, and molybdenum, but exploring alternative materials could open up new opportunities [66, 73, 74, 76, 77]. In conclusion, while ionic liquids and other non-aqueous media offer promising avenues for eNRR, particularly in suppressing unwanted reactions and enhancing nitrogen solubility, further studies are encouraged to confirm these initial experimental results.

3.3 | Li-Shuttle

The process commonly known as lithium-mediated shuttle is an indirect electrochemical synthesis. In this process, ammonia is formed not by nitrogen reduction on the electrode surface but through the reaction of lithium with nitrogen to form lithium nitride. This lithium nitride then reacts with a proton donor to form ammonia. Resulting lithium ions are reduced back to lithium at the cathode, which can again react with nitrogen. Figure 5 shows the corresponding reaction scheme [78, 79].

Organic solvents, such as tetrahydrofuran (THF), are used as electrolytes to limit proton availability and suppress HER. THF is the most common electrolyte due to its high lithium solubility and was used in one of the first publications in this field by Tsuneto et al. [80]. Lithium is added to the system as a lithium salt such as LiOH, $LiClO^4$, $LiBF^4$, and Li_2CO_3, with a concentration of usually 0.2–1 mol/l [10].

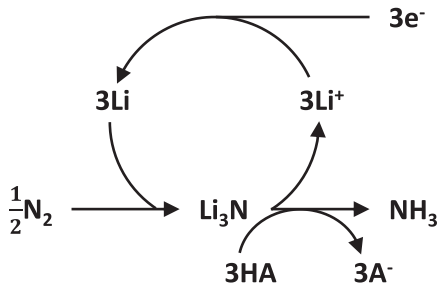

FIGURE 5 | Reaction scheme of the lithium-mediated-shuttle adapted from Krishnamurthy et al. [78] and Gao et al. [79].

While the research field has gained significant attention recently, with many active research groups contributing to its development, it still faces a number of challenges. These are the stability of the electrolyte, the development of an appropriate anode reaction, the transition to a continuous system, enhancement of EE and comprehension of the solid–electrolyte interphase (SEI) [81–84]. Another significant challenge specific to scaling up this technology is the increased demand for lithium. While small-scale experiments require manageable quantities, large-scale applications will demand substantial lithium resources, raising concerns about their availability and sustainability [85]. Waste management and efficient lithium recycling are also critical at industrial scales to minimize environmental impact and reduce costs. Finally, the high consumption of organic electrolytes, such as THF, further compounds these challenges when transitioning from laboratory setups to industrial processes [86].

At the current scale, the identification of a suitable cathode material is important. Precious metals such as gold and silver offer high activity but are costly, whereas non-precious alternatives like copper and molybdenum are more cost-effective and scalable. Copper offers high current densities, while molybdenum achieves high Faradaic efficiencies. Non-metallic materials, such as nitrogen-doped carbon, also show promise due to their efficiency and sustainability [87].

A major issue is the decomposition of THF during electrolysis, which can occur at both the cathode and the anode, initiated by reactions with metallic lithium or oxidation, respectively [81, 88, 89]. Andersen et al. [90] attempted to stabilize the system using a voltage cycling procedure but were unable to fully prevent solvent oxidation. Another approach involved the use of a phosphonium shuttle as a proton carrier, combined with hydrogen oxidation at the anode [91]. Although this method successfully implemented hydrogen in the Li-shuttle pathway and lowered the anode potential, it did not entirely prevent solvent oxidation. Hydrogen oxidation was also implemented recently by Fu et al. [83]. In comparison to Suryanto et al. they used a flow cell system, which was only implemented in a few studies before [86, 92, 93]. They used a more stable anode made of a bimetallic alloy of platinum and gold, successfully avoiding electrolyte decomposition. The work was an important advancement toward establishing a stable and continuous system. However, the high CE of almost 100% demonstrated in previous studies could not be achieved [34, 94].

A major concern with the lithium shuttle process is its low EE. Fu et al. [83] achieved an EE of 13% in their aforementioned study. This figure, while modest, is comparatively high considering early lithium shuttle research reported EE of around 1% [86]. In one of the latest publications in this field, Cai et al. [82] focused their research on enhancing EE by incorporating an MEA. They did not report EE for their system but focused on reducing the cell potential. They achieved a cell voltage of 3.6 V, in contrast to many other studies reporting voltages of 5 V or higher. The work demonstrated the potential of MEAs in lithium-based nitrogen reduction, marking a step forward for this technology. However, the current densities and efficiencies achieved in this MEA system have not yet matched those in systems using liquid electrolytes.

Besides a suitable anode reaction, electrolyte stability, and EE, another crucial aspect of the lithium-mediated shuttle is the SEI. The SEI is an ionically conductive but electrically insulating layer on the working electrode, formed by composition products from electrolyte degradation [90]. This layer segregates the electrolyte from metallic lithium on the cathode leading to diffusion-limited availability of Li, hydrogen, and N_2 at the cathode [95]. Consequently, the SEI significantly influences the achievable CE and current density of the process. It has been observed that the proton donor induces changes of the SEI, thereby altering the diffusion of nitrogen to the electrode [92, 96]. However, the SEI layer and its influencing factors are still not properly understood and require more in-depth research. A major breakthrough in understanding the entire reaction mechanism was the development of a true reference electrode by Tort et al. [95], which could lead to further advancements in the lithium-mediated shuttle process.

Due to the high demand of lithium in other sectors such as transport, research groups are looking for substitutes. Fu et al. [97] introduced a novel approach by substituting lithium with calcium, using $Ca[B(hfip)_4]_2$ in a THF electrolyte mixed with ethanol. They reported a CE of 40% for this system. They used a three chamber cell and implemented hydrogen oxidation reaction at the anode to supply protons. Ethanol was used as a proton shuttle to facilitate the proton transport. Despite observing notable side reactions, such as the formation of calcium hydride (CaH_2) from the reaction of calcium with hydrogen, this system presents a viable alternative to lithium-based methods. The relevance of exploring alternatives like calcium becomes particularly significant in light of lithium's potential limitations, which include its limited availability and high demand in other sectors, such as battery production [85, 98]. The lithium-mediated shuttle process represents a promising but complex method for ammonia synthesis, requiring further innovation in areas like anode reactions and electrolyte stability. Advances in understanding the SEI and exploring alternatives like calcium are encouraging, pointing toward continued progress in this field.

3.4 | Molten Salts

One of the first studies on molten salts as an electrolyte for eNRR was conducted by Murakami et al. [37] in 2003, utilizing a mixture of LiCl, KCl, and CsCl. In their study, ammonia was reported to form through the electrochemical reaction of hydrogen and nitride ions in the system comprised of two nickel gas diffusion electrodes. The nitride ions were continuously produced by the reduction of nitrogen at the cathode. It should be noted that Li_3N was added to the system. Although control experiments were carried out with argon gas and without current applied, the reduction of nitrogen at the electrode was not clearly demonstrated, since the nitrogen from Li_3N can be a nitrogen source for ammonia formation.

Murakami published further work with similar setups. In his publication from 2005, a solid carbon electrode was used for the oxygen evolution reaction by adding water to the system, replacing hydrogen oxidation at the anode [99]. However, instead of O_2, CO_2 was produced at the anode by consuming the electrode. In a subsequent publication, Murakami et al. [100] addressed this issue by implementing a non-consumable boron-doped diamond electrode, preventing the consumption of the electrode.

In further variations of this eNRR system, Murakami et al. introduced hydrogen as a proton source instead of water, leading to the formation of metal sulfides at a nickel anode [17]. By adding HCl instead of water, they additionally demonstrated the possibility of simultaneously producing chlorine gas and ammonia [18]. Murakami also revisited his previously published work, which involved two gas diffusion electrodes. In this variation, methane (CH_4) was used as the gaseous hydrogen source instead of hydrogen [15]. This adaptation represents an exploration of alternative hydrogen sources in the eNRR process.

In all their subsequent studies following the first publication in 2003 [37], Murakami et al. continued to add Li_3N to the electrolyte, such that the nitrogen source for the produced ammonia cannot be unambigouisly determined. This concern is strengthened by a study about the anodic reaction in which Murakami et al. [101] observed that the ammonia production rate is independent of the electrolysis potential.

In 2019, McPherson et al. [102] attempted to replicate the eNRR in a LiCl–KCl molten salt system with the presence of Li_3N. Their conclusion was that the ammonia likely resulted from a non-catalytic reaction between Li_3N and hydrogen, rather than from electrocatalytic reduction of nitrogen. To explore catalytic ammonia production, they modified the experimental setup by replacing Li_3N with LiH and proposed an indirect reduction of nitrogen by lithium for their system similar to the lithium-mediated-shuttle in organic solvents. Their modified setup achieved a production rate of 28 nmol/cm^2/s with a CE of 4.2% over a duration of 2.2 h. This result represented a notable advance in the field, suggesting the feasibility of an alternative pathway for eNRR.

Another lithium-based approach was followed by McEnaney et al. [26]. In their approach, the electrochemical reduction of lithium from LiOH in a molten salt was spatially and temporally separated from the subsequent nitridation by nitrogen and the formation of ammonia by the addition of water. The Li_3N formed during the nitridation of Li reacted with water to form LiOH and ammonia. Ammonia can be separated and the LiOH is reused in the process. The separation of the process steps was implemented to prevent unwanted side reactions of lithium

and thus increase selectivity. Employing this step-wise operating mode, they achieved a remarkable CE of 88.5%.

Beside the Li-based electrolytes Licht et al. [103] attempted to synthesize ammonia in suspension of Fe_2O_3 in a NaOH–KOH molten salt with nickel electrodes. They used N_2 as nitrogen and H_2O as hydrogen source. However, the publication was later retracted when the authors found NO_x^- impurities in their nanoscale Fe_2O_3, unknown at the time of the publication. They concluded, probably in light of findings in LT eNRR, that the produced ammonia likely originated from these impurities rather than from the reduction of N_2.

Following the work by Licht et al., Cui et al. [104] from the same research group conducted a similar experiment but replaced nanoscale Fe_2O_3 with solid Fe_2O_3. They reported a production rate of 8.27 nmol/cm^2/s and a CE of 13.7%. While Cui et al.'s paper bears substantial similarities in experimental setup and materials to the work by Licht et al., there has been no retraction of this publication. Nevertheless, the paper describes the utilization of $Fe(NO_3)$ for catalyst production, which significantly increases the likelihood of system contamination with NO_x^- impurities.

In 2016, Kim et al. [105] combined the approaches of Murakami et al. [15, 17, 18, 37, 99–101] and Licht et al. [103] by using a LiCl–KCl–CsCl electrolyte and Fe_2O_3 particles as nanocatalyst. They achieved a production rate of 0.3 nmol/cm^2/s with a CE of 0.17%, significantly lower than the rates of 20 nmol/cm^2/s at a CE of 23% achieved by Murakami et al. The lower rate in Kim et al.'s work could be attributed to the absence of LiN in their system, suggesting that in previous works using LiCl–KCl–CsCl electrolytes, ammonia formation was primarily formed from Li_3N. To the best of our knowledge, there is no continuation of this work beyond 2020 or other publications on eNRR in molten salts.

Thus, the activation of N_2 in molten salts is challenging, but a lithium-based approach similar to that of the lithium-mediated-shuttle at ambient temperatures could offer a viable route for eNRR. Presumably, the hurdles due to the more complex experimental set-up caused by the required temperatures compared to the LT lithium-mediated-shuttle, have prevented more intensive research to date.

3.5 | Solid Oxide Electrolysis

HT SSAS is typically performed either in proton or oxide-ion conducting electrolysis cells. The operating principle is shown in Figure 6. In proton conducting cells (SOEC-H or PCEC), hydrogen and/or steam is supplied to the anode, which is oxidized to protons. On the cathode side, nitrogen or air are supplied and react to ammonia with the protons and electrons. In oxide-ion conducting cells (SOEC-O), steam and nitrogen are fed to the cathode and are reduced to ammonia and oxide-ions. On the anode side, oxygen is produced.

The first report about electrochemical ammonia production in SOECs was published in 1998 by Marnellos and Stoukides [106]. They performed the electrolysis in a proton conducting cell with platinum electrodes at 570°C and atmospheric pressure and report an ammonia production rate in the order of magnitude 4.5 nmol/s, which was 3 orders of magnitude higher than the conventional catalytic reactor with equal temperature and pressure. Area-normalized values were not reported, but with the given apparent and catalytic surface areas, the production rates can be calculated as 3.5 and 0.056 nmol/cm^2/s, respectively.

Since demonstrating the possibility of electrochemical ammonia synthesis in SOCs, its improvement with respect to the ammonia production rate and CE has been a major topic of research (see Section 4). Topics of interest include the improvement of electrode and electrolyte materials, the investigation of different hydrogen sources and the optimization of operating conditions.

Marnellos and Stoukides [106] addressed the role of proton conduction. Subsequently, different proton conductors were investigated by various research groups. In 2017, Yoo et al. [40] related various reported ammonia formation rates with the proton conductivity of the materials and found an empirical linear relationship between them. An increased proton conductivity generally resulted in an increase in the ammonia formation rate.

Comprehensive reviews of different materials and their respective ammonia formation rates were provided by Amar et al. [107], Qing et al. [108], and Wang et al. [109]. Amar et al. [107] provided the following order of decreasing average ammonia formation rate for various material structures: doped-ceria/phosphate composites > fluorites > perovskites > pyrochlores. However, the reviews [107–109] indicate that the majority of reports were on doped perovskites, and thus, the spectrum of reported ammonia formation rates for these materials is broad.

The highest ammonia production rates in SSAS were reported for doped-ceria/phosphate composites and fluorite-type doped ceria electrolytes [107]. Liu et al. [110, 111] analyzed the doped-ceria composites $Ce_{0.8}M_{0.2}O_{2-d}$ (M = La, Y, Gd, Sm) [110] and $(Ce_{0.8}La_{0.2})_{1-x}Ca_xO_{2-d}$ [111], which showed ammonia production rates in the range of 7–8 nmol/cm^2/s. Wang et al. [38] combined yttrium-doped ceria with calcium and potassium phosphates and obtained the highest reported ammonia production rate in SSAS of 9.5 nmol/cm^2/s at 650°C. In all these publications, the same group of researchers was involved and no new data on these materials have been published since 2006.

The other electrolyte type in SOCs is the oxygen-ion conductor. While this type has been used for decades in steam and carbon dioxide electrolysis as well as in solid oxide fuel cells, it was not until 2009 that Skodra and Stoukides [39] first reported its application in SSAS. For the most common oxygen-ion conducting electrolytes (gadolinium-doped ceria, GDC, and yttrium-stabilized zirconia, YSZ) only a very limited number of publications were published for SSAS [39, 112–115]. Since 2011 the research group around Amar/Tao [116–118] investigates doped ceria–carbonate composite electrolytes for ammonia synthesis. These materials can be both proton and oxygen-ion conducting. In contrast to molten carbonates, the carbonate–oxide composite material remains in the solid state at intermediate operating temperatures. A rather unique feature of their approach is the use of wet air for providing the hydrogen and nitrogen sources, which skips the nitrogen separation and hydrogen production processes prior to ammonia synthesis. However, similar to the remark about the phosphate composite electrolytes, the oxide–

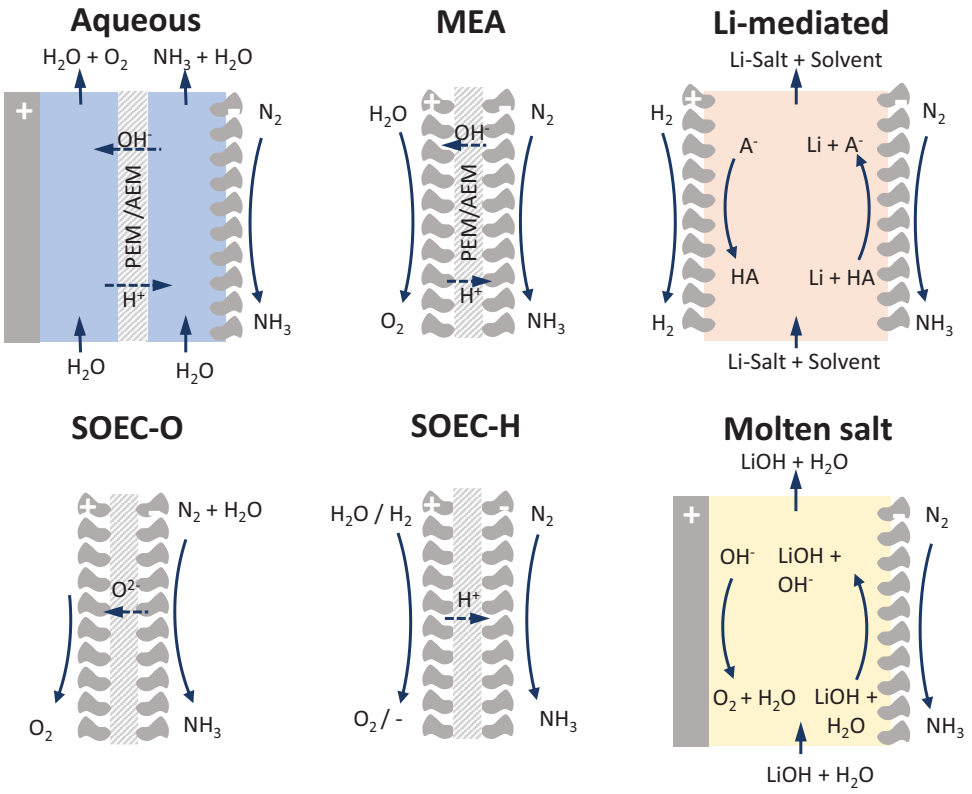

FIGURE 6 | Schematic representation of the reactor expansion for various eNRR technologies. eNRR, Electrochemical nitrogen reduction reaction.

carbonate composites were only investigated by one research group.

Overall, the obtained ammonia production rates in oxygen-ion conductors are lower than in proton conductors. However, given the scarcity of reports, the reason cannot be fully clarified. It could be the generally higher required operating temperatures or the lack of suitable electrode materials and catalysts, which provide good electronic and ionic conductivities and enough catalytic activity toward ammonia formation. Another possibility is the necessity to use steam instead of hydrogen to provide the protons for the ammonia production. While steam would be a preferable hydrogen source (skipping the hydrogen production step, producing oxygen as a side product), it has also shown a low ammonia production rate in the order of magnitude of 10^{-10} to 10^{-12} mol/cm^2/s in proton conducting cells [108]. Again, only a scarce amount of papers were published on using steam instead of hydrogen [39, 117–121].

In addition to electrolyte materials, the electrodes and possible catalysts were explored for improving the ammonia production rate. For many of the early studies that explored various electrolytes, the standard electrode consisted of Ag–Pd (see overview in review of Amar et al. [107]). In the conventional ammonia production, Fe-based catalysts are common and have been tested in SSAS [36, 122, 123]. Other catalysts or electrode materials that were explored in literature include Co_3Mo_3N [115, 124], Fe_3Mo_3N [125], perovskites [118–120], Ru-modified perovskite [114, 126], Ni-BCY cermet [121], Spinel [116]. The comparison of catalyst and electrodes materials is rather difficult, since most of the groups use different electrolytes. One systematic analysis of different electrodes with the same electrolyte was made by Yun et al. [120] and only in such an approach the effectiveness of the electrode or catalyst material can be evaluated.

A similar remark has to be made with respect to operating conditions like temperature, current (density), and potential. Many papers report a volcano type relationship between the ammonia production rate and temperature [110, 127–131], meaning that there is an optimal temperature below and above which the production rate drops. Lower temperatures reduce the reaction kinetics, while at higher temperatures ammonia is increasingly decomposing. There does not seem to be a general agreement on an optimal temperature. It might depend also on the materials that are used or the current that is applied.

The concerns of false positive ammonia detection were raised in recent years. For the SSAS literature, this topic has not been addressed in detail but the general remarks seem comparable. Wang et al. [109] provided a comprehensive overview of the SSAS literature with the respective detection method and control experiments. The majority of reports seem to use Nessler's reagent to detect the ammonia production. In contrast to liquid-phase ammonia synthesis, SSAS could make use of gas chromatography to determine the ammonia production rate, however, only the groups of Stoukides and Vayenas [36, 106, 122, 132] seem to reportedly use it. Ouzounidou et al. [122], however, reported that GC is not reliable if the concentration of hydrogen and N_2 are high and their conversion low. There is an interference of steam and ammonia. Other techniques to measure ammonia include cavity ring-down spectroscopy [133–135], HPLC [123, 136] and an NH_4^+ ion-selective electrode [117, 118, 137–139]. If control experiments

are done, they consist of tests at open circuit voltage, without current and thus no electrochemical ammonia production should take place. In those cases, it is typically reported that no ammonia is detected.

Ammonia production in solid oxide cells is difficult as the raised temperature favors ammonia decomposition. Novel catalyst materials like doped-ceria/phosphate composites provide promising results for increasing the production rate, however, their effectiveness has yet to be confirmed by more research groups and more effort is still needed in improving those materials to obtain industrially viable production rates. Additionally, the ammonia detection has to be improved to include the proposed blind tests to ensure that the detected ammonia is indeed coming from the intended reaction.

4 | Key Performance Indicators

To date, there has not been a comprehensive review that integrates the various technologies across the different research domains of eNRR. One contributing factor may be the differing terminology used in these fields. For instance, in the lithium-mediated shuttle field, terms such as 'lithium-mediated' are commonly associated with 'nitrogen reduction' or 'ammonia synthesis.' In aqueous eNRR, the phrases 'electrochemical nitrogen reduction' and 'electrochemical ammonia synthesis' are more prevalent. Although these terms are also used in HT contexts, they are often modified with descriptors like 'proton conduction,' 'solid state,' or 'atmospheric pressure.'

Moreover, the comparability of these technologies is challenging due to the different key performance indicators (KPIs) that are defined and measured in the HT and LT domains, making direct comparisons difficult. This inconsistency in terminology and KPI measurement may contribute to the lack of comprehensive coverage of HT applications in many eNRR reviews. Furthermore, the relatively lower number of publications in the HT eNRR field compared to the LT field, which can be attributed to the significantly higher experimental effort required for HT electrolysis cells, presents an additional challenge for conducting a thorough review. The following comparison will evaluate the different technologies based on the KPIs production rate, CE, and EE.

4.1 | Production Rate

The production rate is probably the most common key performance indicator used in the field of eNRR. In contrast to other research areas, such as CO_2 reduction, where terms like CE, polarization curves, or EE are employed [140], the specific area production rate is frequently used as the comparative metric in the field of eNRR. This is primarily because in eNRR, except for the lithium shuttle, the achieved production quantities are small. Thus, the production rate becomes a critical metric for demonstrating the feasibility of synthesizing ammonia from nitrogen, with the achieved efficiency taking a secondary role. The production rate is typically expressed in surface-normalized units, using the unit mol/cm^2/s, where the area corresponds to the electrode's geometric surface area [141–143]. Some reports

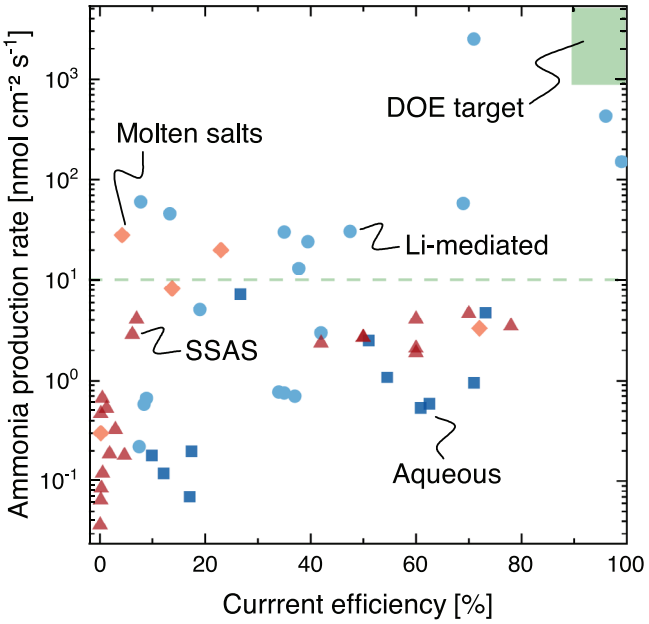

FIGURE 7 | Literature result for aqueous (■), lithium-mediated (•), molten salt (◆), and SSAS (▲) eNRR. The green area marks the range that the US Department of Energy has defined as the target value for the eNRR [47]. The line represents the lower limit of Choi et al. [13] for "highly plausible and promising" results.

express the production rate per mass of catalyst (mol/cm^2/mg$_{cat}$) which makes a direct comparison difficult especially when the catalyst loading of the electrode is not reported. In SSAS research, both geometric and active catalyst surface areas are used to calculate the ammonia production rate, making a direct comparison difficult [9, 144, 145]. Given the current TRL of eNRR, the production rate remains a crucial parameter for evaluating system performance. It allows for comparison between different techniques and provides insights into the reliability of measurements. Therefore, it is advisable for future publications in the eNRR field to continue utilizing the production rate as a primary metric for assessment and comparison. However, for improved consistency and comparability, a standardized unit based on easily determinable parameters should be employed. The method of measurement can introduce errors in determining both the active surface area and actual catalyst surface area of an electrode. Hence, we suggest uniform measurements based on the geometric surface area of the electrode, as it is straightforward to determine and introduces fewer uncertainties. Additionally, it is also the more relevant parameter for future industrial applications.

Figure 7 shows reported production rates and current efficiencies for aqueous, lithium-mediated, molten salt and SSAS eNRR. For aqueous systems, all studies that were classified 'very likely reliable' by Rezaie et al. [10] as well as in this review reported lithium-mediated approaches are included.

In the case of molten salts, all non-retracted publications reporting CE and production rate are considered. For SSAS, data from three comprehensive reviews [107–109] are taken into account, but only those providing both ammonia production rate and CE are presented. In case of multiple value pairs, both the one

with the highest ammonia production rate and the one with the highest CE are considered. The highest ammonia production rate in the literature is 9.5 nmol/cm^2/s [146], however, no CE was provided and thus this value is not included in our figure.

Comparing the reported production rates one can see that the rates for SASS are, together with aqueous systems the lowest among all with no study exceeding 10 nmol/cm^2/s. For aqueous systems, the values are in the range of 2 orders of magnitude with several reports of production rates between 1–10 nmol/cm^2/s. Despite the extensive number of studies already conducted, significant advancements in aqueous systems seem unlikely without a major breakthrough. In contrast, SASS has been less explored, possibly due to the higher experimental demands of an HT setup. From our perspective, this technology therefore holds comparatively greater potential. However, results for both field fall below the threshold set by Choi et al. [13] as highly plausible and promising in terms of being free from false positives (dotted line). Molten salts demonstrate slightly higher rates and are the least explored field, offering significant potential for further development. Lithium mediated eNRR represent the newest area where production rates typically range between 10–100 nmol/cm^2/s. An exception is the study by Li et al. [94], reporting a high yield of 2500 nmol/cm^2/s, exceeding all other results by an order of magnitude. Some studies in this field report production rates and current efficiencies close to the targets set by the US Department of Energy for industrial applications [47]. Despite being the newest research area, it offers the most promising and plausible results with the greatest potential for industrial-scale implementation.

The production rate is not the only, but probably the most critical KPI currently, as it serves both as an indicator of performance and as a means of avoiding false positive results. With proof of principle and increasing TRLs, CE also plays a crucial role, which will be discussed in the following chapter.

4.2 | Current Efficiency

The CE is a critical performance indicator in electrochemical processes, as it describes the selectivity of the catalyst [147]. The achieved CE varies among different eNRR technologies, as shown in Figure 7. For SSAS the CE is low, not exceeding 10%. It shall be noted that CE in the field of SSAS is often not reported, limiting the number of studies included in the graph. For molten salts, the CEs achieved are also low, with the exception of a study by Murakami et al. [37], where a CE of 72% was achieved in their initial publication. The highest CE of 88.5%, reported by McEnaney et al. [26] is not included due to the absence of a comparable production rate for the discontinuous system. No clear trend can be identified for aqueous systems as both very low CE values of 10% and others exceeding 70% are reported. The same applies to lithium-mediated systems, for which a large range of 13%–99% can be found in the literature, whereby the high CE are achieved at significantly higher production rates and thus current densities compared to the other technologies. In other areas of electrochemical synthesis, such as CO_2 reduction, there is often a correlation between the applied current density and the resulting CE [148, 149]. However, in the field of eNRR, few studies have specifically addressed mass transfer limitations [150]. Exceptions include the study by Liu et al. [150], which developed a new reactor to enhance mass transport, and the work by Lazouski et al. [86], who developed a kinetic-transport model for the lithium-mediated shuttle.

One reason for this is that, except for the lithium-mediated pathway, the aim so far has been to prove the feasibility of eNRR. Additionally, aside from the lithium-mediated pathway, current densities have remained low. In lithium-mediated eNRR, a universal correlation between current density and CE has not been established, potentially due to the relatively short existence of this research field. Future investigations are expected to address this aspect. In SSAS, the CE is mostly referred to as 'Faradaic efficiency', but its usage is not consistent across the literature. In early studies, where electrical ammonia synthesis was often compared with catalytic ammonia synthesis, a phenomenon called non-Faradaic electrochemical modification of catalytic activity (NEMCA) has been reported [132, 151, 152]. The effect describes an additional increase of (non-Faradaic) catalytic activity when ions are provided electrochemically. The enhancement is described by a dimensionless enhancement factor lambda, which is defined as the ratio of the increase of the catalytic rate either of consumed reactant [36, 122, 132] or formed product [153] and the rate of electrochemically provided reactant or product, respectively. A lambda value greater than one indicates the presence of a NEMCA effect. This enhancement factor is often referred to as 'Faradaic efficiency', although this is misleading as it actually describes the non-Faradaic enhancements. Instead, the term 'Faradaic efficiency' should be used for the conventional definition established in electrochemistry as described above. In case of double-chamber cells, where hydrogen is not fed to the cathode (most electrolysis cells), there is no NEMCA effect and thus the enhancement factor describes the Faradaic efficiency.

The variation in CE (or Faradaic efficiency) across different eNRR methods emphasizes the complexities in electrochemical ammonia synthesis and the importance and requirement of ongoing research.

4.3 | Energy Efficiency and Polarization Curves

As described above, polarization curves and EE in areas such as CO_2 reduction or water electrolysis, which have already reached a high TRL, are essential KPIs [140]. Polarization curves illustrate the relationship between cell voltage and current density and offer comparability of different cell types with respect to a specific reaction. In processes with side reactions, it is important to define the current density as a product-specific current density to ensure comparability. EE is calculated as the ratio of the reversible cell voltage and the actual cell voltage [154].

$$\mathrm{EE} = \frac{U_{\mathrm{reversible}}}{U_{\mathrm{actual}}} \tag{6}$$

In the presence of the side reaction, the CE has to be considered and the EEis defined as [140].

$$\mathrm{EE} = \frac{U_{\mathrm{reversible}} * \mathrm{CE}}{U_{\mathrm{actual}}} \tag{7}$$

In eNRR, polarization curves and EE are primarily relevant in the lithium-mediated pathway at the moment. As mentioned earlier, other technologies remain at the proof-of-principle stage. However, as soon as elevated production rates are reliably achieved, the focus must be broadened to design energy efficient cells. In the domain of lithium-mediated eNRR, EE is gaining significance. The proof of principle has been established, despite ongoing technical challenges, leading to an increasing optimization of process parameters. Consequently, several publications now address EE, with reported values ranging from 1.4% to 14% [83, 87, 88, 90, 93, 94]. It should be mentioned here that only the electricity used and not the sacrificial proton source was considered when calculating the energy efficiency. This focus on energy efficiency in the lithium-mediated pathway reflects a maturing, field where researchers are not just proving feasibility but also optimizing for practicality and scalability.

5 | Techno-Economic Analysis and Life-Cycle Assessment

Techno-economic analyses (TEA) play an important role in research by offering a systematic framework to evaluate the economic viability and potential impact of new technologies, guiding researchers in their exploration of innovative solutions. TEA help scientists and academics to make informed decisions about which research directions to explore further. TEA are valuable not only for processes with high TRL but also for those at lower TRLs, as they allow the assessment of economic viability and identify areas for improvement of emerging technologies [155]. This helps bridge the gap between innovation and practical application. For this reason, TEA in the field of eNRR are particularly beneficial for identifying critical parameters and quantifying the necessary performance parameters that must be achieved in order to enable economical production in the future. In addition, based on predictions about future performance, a comparison can be made between different technologies.

Various studies have focused on TEA of eNRR with different technologies [4, 8, 156–162]. Lazouski et al. [156] recently published a study that adopts a generalized approach to identify research goals in eNRR. They modeled a process with four unit operations: air separation to produce N_2, electrochemical water splitting to generate hydrogen, the electrochemical synthesis of ammonia from hydrogen and N_2 (green HB) and ammonia separation. They optimized the process toward hourly variations in electricity supply and a production capacity of 250 tonnes ammonia per day. The calculated ammonia price was 900–1000 US$ per tonne ($/$t_{NH_3}$). Additionally they identified minimum technical parameters that need to be achieved, in particular a current density of 400 mA/cm^2 and an energy efficiency of >32%. From the minimum required energy efficiency they calculated a maximum acceptable overpotential of 2.45 V at a CE of 100%. The authors concluded that the lithium-mediated pathway requires fundamental modifications as the reported overpotentials for this technology exceed 3 V in existing publications.

Hochmann et al. [8] compared aqueous electrochemical ammonia synthesis with two HB based processes. One with electrochemically produced hydrogen (green HB) and a second conventional HB process with hydrogen based on fossil resources (conventional HB). They assumed a production rate of 282 metric tonnes of ammonia per day (t_{NH_3}/day) with an energy efficiency (EE) of 62.2% for the electrochemical process. The calculated costs for the production of ammonia by the electrochemical process was calculated to 508 US$/$t_{NH_3}$. The authors concluded that if CO_2 costs are considered, the renewable power-based eNRR would be economically competitive at this EE. In fact, it could be even more economical than a green HB process at 80% EE. However, they state that current eNRR technology is far from reaching these high efficiencies and that today only the green HB process is an alternative to the conventional HB process.

Gomez et al. [161] focused on the comparison of different hydrogen supplies for the electrochemical conversion of hydrogen and N_2 to ammonia and compared this to a green HB process. They compared four different hydrogen sources: methane steam reforming, methane steam reforming with CO_2 capture, solid oxide electrolysis, and polymer electrolyte membrane electrolysis. They assumed the US department of energy targets (90% CE, 300 mA/cm^2, 930 nmol/s/cm^2) as parameters for eNRR and calculated ammonia costs between 951 and 1437 US$/$t_{NH_3}$ for a production of 140 t_{NH_3}/day [47]. These cost estimates are similar to those calculated by Lazouski et al. [156].

The most cost effective process was the polymer membrane-based hydrogen production followed by the solid oxide based system. Both were slightly more economical than the calculated green HB process. Gomez et al. [161] highlighted the advantage of the electrochemical process in terms of linear scalability compared to conventional ammonia production methods. This was investigated by Fernandez et al. [160] who focused on the economic effects of the production scale. They compared a conventional HB, green HB, eNRR based on electrochemically produced hydrogen (two-stage eNRR), and eNRR based on nitrogen and water (single-stage eNRR) for production rates of 2000 and 0.03 t_{NH_3}/day. They concluded that with electricity prices of 0.03 US$/kWh electrochemically based systems cannot reach current production costs of 159 US$/$t_{NH_3}$. The single-stage eNRR production costs were calculated to 750 US$/$t_{NH_3}$ and the two-stage eNRR to 420 US$/$t_{NH_3}$. They noted that production costs are dependent on scale, and decentralized production could be beneficial for electrochemical processes. The authors calculated the price parity for a single-stage eNRR at a rate of 4 t_{NH_3}/day and for a two-staged eNRR at a rate of 30 t_{NH_3}/day, meaning that below these values the eNRR process would be more economical than HB. For a small-scale, decentralized production rate of 0.03 t_{NH_3}/day, suitable for fertilizing 100 hectares [160], the single-stage and two-stage costs were calculated to be 910 and 510 USD/t_{NH_3}, respectively. At this scale, additional costs for transportation and storage are eliminated, making these processes more competitive compared to the centralized HB production. Another important finding stated by Fernandez et al. [160] is that if CO_2 costs are taken into account, the direct two-stage eNRR, reaching 430 US$/$t_{NH_3}$, could be economical favorable to a green HB process at 480 US$/$t_{NH_3}$. The slight difference to the value of 508 calculated by Hochman et al. [8] is caused by different assumptions in the economic evaluation. However, given the large number of parameters influencing the results, they are in a comparable range. Fernandez et al. set a

target of 100 mA/cm^2 at a CE of 48% and 13% for single-stage and two-stage eNRR, respectively, assuming LT.

While most available TEA focus on LT aqueous systems, Gomez et al. [157] investigated a lithium-mediated process in addition to their study on various hydrogen supplies for a proton-conducting eNRR [161]. They assumed a process where LiOH is consumed at the anode to provide Li^+ ions with water and oxygen as side products. The Li^+ ions then form Li_3N with N_2 at the cathode which reacts with water to LiOH and ammonia. The LiOH is then recycled. They assumed a cell voltage of 3 V, 80% CE and a 90% conversion efficiency of nitrogen to ammonia. Based on these assumptions, the production costs were calculated to 695 US\$/t_{NH_3} at a production rate of 154 t_{NH_3}/day. This cost is lower than the calculated costs for eNRR based on proton conducting membranes (951 US\$/t_{NH_3}), green HB processes (975 US\$/tNH_3), and conventional HB processes (710 US\$/t_{NH_3}) at the same scale. They additionally calculated the energy demand to 23 MWh/t_{NH_3} which is 23% less compared to a system with a proton conducting membrane [157].

In summary, there are TEAs, especially for eNRR at LTs, which provide a comparison with the competing incumbent processes, which are the conventional HB process or the green HB process, and provide targets for future eNRR. This shows that the LT eNRR has potential for an economical process, but that current research is still far from achieving those targets. There are initial estimates for the relatively new lithium-mediated technology that indicate the potential economic viability of the process, whereby energy efficiency in particular represents a major challenge due to the high excess potential currently required. To date, there is no comprehensive TEA for HT applications. For this technology, an economic analysis that compares the HT applications molten salts and solid oxide electrolysis with the lithium-mediated process and considers various downstream processes for purifying ammonia would be of particular interest.

6 | Latest Achievements and Future Challenges

The progress made in various eNRR technologies differs greatly, mainly due to their distinct levels of development and the varying number of studies conducted in each area.

In the field of aqueous eNRR, it has become apparent in recent years that many of the earlier studies might have incorrectly attributed the reduction of N_2 to ammonia, not considering unknown contaminants or nitrogen sources at that time. The development of experimental protocols in response to these findings has significantly advanced the research field. Nevertheless, it has been observed that the risk of false positive results due to minor impurities remains, meaning that true nitrogen reduction can only be confidently affirmed when higher production rates are achieved, effectively ruling out contamination or conversion of NO_x [13, 75]. We suggest that experiments should be replicated in different laboratories by various operators to eliminate possible errors caused by the specific setups or individual operators. Unfortunately, a considerable number of publications still do not align with the current state of knowledge in this field. Thus, the most pressing challenge in the field of aqueous NRR is to reach a production rate which allows for unambiguous interpretation of the results.

In the field of non-aqueous systems (with the exception of lithium mediated shuttle), the number of publications is significantly lower and the studies carried out were predominantly conducted before the discovery of potential false positive results in aqueous eNRR. Non-aqueous systems, particularly those involving ionic liquids, present potential advantages such as increased N_2 solubility, inhibition of the HER, and increased thermal stability or operating temperature range [163]. However, non-aqueous systems are also subject to uncertainties regarding false positive results, with the introduction and conversion of NO_x in the system being particularly critical. To the best of our knowledge, no studies have been conducted to date that have demonstrated N_2 reduction in non-aqueous LT systems (with the exception of lithium-mediated). Similar to the approach in aqueous LT electrolysis, studies in non-aqueous systems should include control experiments that align with the current state of scientific knowledge and achieve sufficiently high production rates. These experiments would need to be replicated in various laboratories by different operators to conclusively prove the feasibility of N_2 reduction to ammonia in non-aqueous LT systems.

The most promising LT application for N_2 reduction is the lithium-mediated shuttle. The proof-of-principle stage has already been overcome, shifting the focus on in depth understanding of the reaction system, stable proton supply without sacrificial conversion of the electrolyte, and increasing production rate, CE, and energy efficiency [90, 98]. With regard to an industrial application, achieving a sufficiently low cell voltage of less than 3 V is crucial [156]. Latest approaches aim to reduce the cell voltage via an MEA, where 3.6 V has already been achieved at a low CE [82]. Ahmed et al. [98] pointed out that the supply of raw materials as lithium could be challenging for a large-scale industrial application. In particular, a conflict of interest with other important large-scale industries such as battery production could lead to supply chain constraints and price fluctuations. Another critical aspect, which has received limited attention so far, is the purification of ammonia. The development of advanced purification or separation technologies is essential for a viable industrial process [164]. Alongside economic considerations, the ecological impact of using organic solvents as electrolytes in the lithium-mediated shuttle must be taken into account [98]. The possibility of generating toxic by-products necessitates strategies for their safe disposal, especially in a process aimed at scaling to levels comparable to the HB process. Despite the major challenges, the lithium-mediated shuttle is the only LT eNRR method to date with sufficiently high production rates and offers the prospect of potential industrial application. Its advancement represents a critical step toward sustainable ammonia production, but it requires careful consideration of both economic and environmental factors.

In HT eNRR, the two different technologies are molten salts based on liquid electrolytes and SSAS based on solid electrolytes. Studies on molten salts essentially date from a time when the possibility of false positive results due to contamination were not known. These findings led to the retraction of one study from this field, as the authors identified NO_x as a source of nitrogen

[103]. Several other studies in this area are based on the work of a research group whose efforts have not been continued since these new findings emerged and, to the best of our knowledge, have not been validated.

An approach based on indirect nitrogen reduction via lithium, like the lithium-mediated shuttle, has been shown for molten salts in two different approaches [26, 102]. To the best of our knowledge, no further work on the use of lithium in molten salts has been published since then. Despite the promising results achieved in the LT lithium-mediated shuttle, the potential of using lithium in molten salts remains largely unexplored. This area could benefit from further investigation, particularly to determine if molten salts can prevent electrolyte degradation, the impact of the SEI layer in the system, and the feasibility of implementing a sustainable proton source. Additionally, a comparison of energy efficiency and the potential reduction in cell voltage due to elevated temperatures would be of interest. One disadvantage of the HTs could be the thermal decomposition of ammonia into nitrogen and hydrogen. The decomposition reaction of ammonia reaches almost full conversion at 450°C, which falls within the typical temperature range of molten salt systems [25, 165].

Most studies conducted in SSAS were published before possible false positive results in aqueous systems became known, which is important for understanding the state of current research. In contrast to all other technologies in SASS no liquid electrolyte is used and all reactants and products are in a gaseous state due to the HTs which usually exceed 500°C [108, 109]. In SSAS, oxygen ion and proton conducting electrolytes are used. Proton conducting electrolytes have been identified as most suitable and the production rate is related to the proton conductivity. A high proton conductivity leads to higher production rates [40, 106]. A major challenge in SSAS is finding effective catalysts or electrode materials that can enhance ammonia production rates while suppressing hydrogen evolution, thereby allowing for the use of higher current densities. Catalysts should be compared using the same electrolyte to evaluate the effectiveness of the electrocatalytic activity. Similar reaction conditions would be preferable, however, the optimal conditions might be depending on the materials used, since ammonia tends to decompose at higher temperatures. Thus, at HTs there is always a trade-off between sufficiently HT to ensure good kinetics toward ammonia production (higher ionic conduction at higher temperatures, overall faster reaction kinetics) and ammonia decomposition at higher temperatures. To date, the production rates and CE achieved in SSAS are comparable to those in aqueous systems. However, the possibility of false positives has hardly been considered so far. Most of the causes of alternative origins of ammonia formation known from LT eNRR can also occur in HT SSAS. In particular, the contamination of the gas source with ammonia and NO_x, the absorption and subsequent conversion of NO_x on the catalyst or reactor surface, or the conversion of nitrogen-containing catalysts should be considered. Since no polymer membrane is used in SSAS, it can be ruled out as a source of ammonia, but whether ceramic electrolytes absorb or desorb ammonia remains, uninvestigated. The focus on control experiments should be significantly increased as critical tests like ^{15}N experiments are usually not conducted. Another challenge for a later industrial application of SSAS is the stability of the electrolytes, a concern already highlighted in other applications with higher TRLs [166].

When comparing LT and HT applications in eNRR, a notable advantage of LT applications should be underscored. While the anode reaction poses a challenge in the LT scenario, it is feasible to implement a value-adding reaction at the anode, instead of the oxygen evolution reaction. In HT applications, possible reactions are limited since the resulting products must be temperature-stable. This limitation could present a significant advantage for LT applications, where the implementation of a value-adding anode reaction can greatly enhance economic potential [167, 168].

7 | Summary and Outlook

The entire field of eNRR is facing significant challenges. Recent years of research have underscored the need to rethink how research findings are published. Particularly in aqueous eNRR, there are still publications that do not align with the current state of science. This influx of publications, which often fail to adequately address or even acknowledge the issue of false positives in eNRR, creates a cluttered research landscape. This makes it challenging for researchers to discern truly groundbreaking or relevant studies. Consequently, this situation can mislead scientists, especially those new to the field, as they might rely on findings that do not accurately represent the current state of eNRR research or its challenges.

In the research areas of molten salts and SSAS, as well as in non-aqueous liquids, the majority of studies were published before the awareness of false positive outcomes. Consequently, it becomes challenging to draw definitive conclusions from these studies, as their results might have been influenced by unrecognized contaminants or other sources of error. A thorough review of results, especially in these research fields, is of crucial importance.

An exception is the lithium-mediated shuttle, where the proof of principle has been successfully demonstrated. This may also hold true for lithium-based systems in the molten salts domain, although the available data are currently insufficient for a conclusive assessment.

When comparing LT and HT approaches two key aspects are important: temperature impact and reaction rate. Higher temperatures can increase the reaction rate, a principle utilized in the HB process. However, a major disadvantage of HTs is the tendency to decompose ammonia. In addition, the voltage required increases with rising temperatures as shown in Figure 1 while it decreases for the main side reaction, the hydrogen formation reaction. In SSAS, HTs are essential to ensure sufficient proton conductivity of the electrolyte. However, operating at a temperature that supports ionic conduction while preventing ammonia decomposition presents a significant challenge. Lithium-based molten salt systems might offer a promising alternative to LT lithium-mediated shuttles, particularly if they can address key issues such as the use of sacrificial electrolytes, insufficient proton supply, and high cell voltage. The overarching challenge in eNRR still lies in the development of suitable catalysts. However, it is crucial that research aligns with the current state of literature. The only exception so far is the lithium-mediated technology demonstrated

in molten and organic solvents. Currently, this technology has the greatest potential in the field of eNRR to achieve industrial application with promising prospects for future developments.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Data Availability Statement

No new data were created or analyzed in this study. Data sharing is not applicable to this review.

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